

## A Model Study of Photoinduced Reoordination in Cationic Complexes of Photochromic Azacrown Ethers

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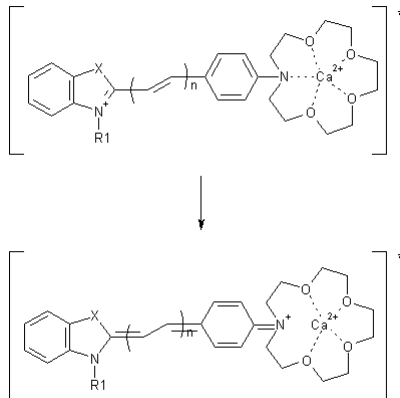
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## A model study of photoinduced recoordination in cationic complexes of photochromic azacrown ethers

Crown ether styryl dyes are known to undergo photoinduced trans-cis isomerization or [2+2]-cycloaddition [1]. Complex formation with metal cations affects the efficiency of these reactions. On the other hand, complex formation of these dyes is photocontrolled, which makes possible the use of these systems as sensors or molecular machines. An interesting case of photoinduced changes was observed in styryl and butadienyl dyes containing N-phenylazacrown ether moiety (see figure). UV absorption spectra of the dyes indicate that photoinduced recoordination occurs in their complexes with metal cations; that is, M--N bond breaks, and the cation moves from the position in the center of the cavity towards the oxygen atoms [2, 3]. Theoretical consideration shows that this recoordination is necessarily followed by a conformational change. Moreover, the recoordination cannot be observed if the conformation of the crown ether moiety is constrained. It is believed (and supported by  $^1\text{H}$  NMR studies) that recoordination and conformational change are caused by electron density redistribution upon photoexcitation.



One can see that the participation of the quinoid resonance form should induce the charge transfer from the heterocyclic N atom to the N in the crown ether thus reducing the binding capacity of the latter. To simulate these changes, the following molecules were taken as models: (1) N-phenylaza-15-crown-5 and (2) its quinoid analog.

Our experience of application of different methods to crown ethers [4] shows that a reliable conformational study is possible using rough *ab initio* methods (like RHF/3-21G), whereas the detailed study of complex formation including formation energies is possible only when the electron correlation is included (MP2/6-31G\*, DFT). However, neither semiempirical nor molecular mechanical simulations can give us the insight into the problem. Therefore, we chose the large-core SBK pseudopotential basis set for our RHF calculation.

It was found that (1) $\text{Ca}^{2+}$  complex assumes the "axial" conformation with the phenyl ring in the axial position to the average plane of the crown ether and has five binding sites, whereas (2) $\text{Ca}^{2+}$  complex assumes the "equatorial" conformation with the phenyl ring in the equatorial position to the crown ether plane and has four binding sites. The axial conformation of (2) $\text{Ca}^{2+}$  also exists but lies  $\sim 4.4$  kcal/mol higher. The fact that (2) $\text{Ca}^{2+}$  has only four binding sites explains its lower formation energy as compared to (1) $\text{Ca}^{2+}$ . This is consistent with the stability constants found for the cation--dye complexes and compared to those for N-phenylaza-15-crown-5.

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